Restoration of the Derivative Discontinuity in Kohn-Sham Density Functional Theory: An Efficient Scheme for Energy Gap Correction

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From the perspective of perturbation theory, we propose a systematic procedure for the evaluation of the derivative discontinuity (DD) of the exchange-correlation energy functional in Kohn-Sham (KS) density functional theory, wherein the exact DD can in principle be obtained by summing up all the perturbation corrections to infinite order. Truncation of the perturbation series at low order yields an efficient scheme for obtaining the approximate DD. While the zeroth-order theory yields a vanishing DD, the first-order correction to the DD can be expressed as an explicit universal functional of the ground-state density and the KS lowest unoccupied molecular orbital density, allowing the direct evaluation of the DD in the standard KS method without extra computational cost. The fundamental gap can be predicted by adding the estimated DD to the KS gap. This scheme is shown to be accurate in the prediction of the fundamental gaps for a wide variety of atoms and molecules.

Over the past two decades, Kohn-Sham density functional theory (KS DFT) [1] has become one of the most powerful theoretical methods for studying the ground-state properties of electronic systems. As the exact exchange-correlation (XC) energy functional $E_{xc}[\rho]$ in KS DFT remains unknown, functionals based on the local density approximation (LDA) and generalized gradient approximations have been widely used for large systems, due to their computational efficiency and reasonable accuracy. However, owing to their qualitative failures in a number of situations [2–5], resolving these failures at a reasonable computational cost continues to be the subject of intense research interest.

The prediction of the fundamental gap E_g has been an important and challenging subject in KS DFT [6–21]. For a system of N electrons (N is an integer) in the presence of an external potential $v_{ext}(\mathbf{r})$, E_g is defined as

$$E_g = I(N) - A(N), \tag{1}$$

where $I(N) = E(N-1) - E(N)$ is the vertical ionization potential and $A(N) = E(N) - E(N+1)$ is the vertical electron affinity, with $E(N)$ being the ground-state energy of the N-electron system. Therefore, E_g can be extracted from three KS calculations for the ground-state energies of the N- and $(N \pm 1)$-electron systems. However, such multiple energy-difference calculations are inapplicable for the prediction of fundamental band gaps of solid-state systems [6–11,14,17,18].

By contrast, the KS gap Δ_{KS} is defined as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the N-electron system [22–24],

$$\Delta_{KS} = \epsilon_{N+1}(N) - \epsilon_N(N), \tag{2}$$

where $\epsilon_i(N)$ is the ith KS orbital energy of the N-electron system. Therefore, Δ_{KS} can be obtained from only one KS calculation for the KS orbital energies of the N-electron system. Note that E_g is not simply Δ_{KS} but is given by

$$E_g = \Delta_{KS} + \Delta_{xc}, \tag{3}$$

where

$$\Delta_{xc} = \lim_{\eta \to 0^+} \left\{ \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{N+\eta} - \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \bigg|_{N-\eta} \right\} \tag{4}$$

is the derivative discontinuity (DD) of $E_{xc}[\rho]$ [23–32]. As the KS gap (even with the exact functional) severely underestimates the fundamental gap [24,25,31], the evaluation of the DD is tremendously important. Recently, the importance of the DD in the excited-state [33] and time-dependent [34,35] properties has also been highlighted. Although several schemes have been proposed for calculating the DD, they can be very computationally demanding for large systems, due to the use of the nonlocal energy-dependent self-energy operators [6,7,10,11,18] or of the Hartree-Fock operator [8,13,21].

In this Letter, we provide a systematic procedure for the evaluation of the DD, based on perturbation theory [36]. The lowest-order estimate of the DD can be expressed as an explicit universal (i.e., system-independent) functional of the ground-state density and the KS LUMO density, allowing very efficient and accurate calculations of the DD and, via Eq. (3), the fundamental gap in the standard KS method.

For the exact KS DFT, $I(N) = -\epsilon_N(N)$ [22,23,28,37–39], and therefore $A(N) = I(N+1) = -\epsilon_{N+1}(N+1)$. Consequently, E_g [see Eq. (1)] can be expressed as

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N), \tag{5}$$

which is simply the energy difference between the HOMOs of the N- and $(N+1)$-electron systems [26]. By subtracting Eq. (2) from (5), Δ_{xc} [see Eq. (3)] can be expressed as

$$\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N)$$
$$= \langle \tilde{\psi}_{N+1} \mid \tilde{H}_{KS} \mid \tilde{\psi}_{N+1} \rangle - \langle \psi_{N+1} \mid H_{KS} \mid \psi_{N+1} \rangle. \tag{6}$$

Here, $H_{KS} \equiv \{-\frac{\hbar^2}{2m_e}\boldsymbol{\nabla}^2 + v_{ext}(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}([\rho];\mathbf{r})\}$ and $\psi_i(\mathbf{r})$ are, respectively, the KS Hamiltonian and the ith KS orbital of the N-electron system, with $v_{xc}([\rho];\mathbf{r})$ being the XC potential and $\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$ being the ground-state density. $\tilde{H}_{KS} \equiv \{-\frac{\hbar^2}{2m_e}\boldsymbol{\nabla}^2 + v_{ext}(\mathbf{r}) + e^2 \int \frac{\tilde{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}([\tilde{\rho}];\mathbf{r})\}$ and $\tilde{\psi}_i(\mathbf{r})$ are, respectively, the KS Hamiltonian and the ith KS orbital of the $(N+1)$-electron system, with $v_{xc}([\tilde{\rho}];\mathbf{r})$ being the XC potential and $\tilde{\rho}(\mathbf{r}) = \sum_{i=1}^{N+1} |\tilde{\psi}_i(\mathbf{r})|^2$ being the ground-state density.

Aiming to compute Δ_{xc} (and hence E_g) using only one KS calculation for the N-electron system (e.g., for being applicable to solids), we express $\epsilon_{N+1}(N+1)$ in terms of $\{\epsilon_i(N), \psi_i(\mathbf{r})\}$, based on perturbation theory [36].

We choose H_{KS} as the unperturbed Hamiltonian and suppose that the unperturbed energy levels are nondegenerate. Let λ be a dimensionless parameter, ranging continuously from 0 (no perturbation) to 1 (the full perturbation). Consider the perturbed Hamiltonian H_λ given by

$$H_\lambda = H_{KS} + \lambda H'_\lambda, \tag{7}$$

where the perturbation $H'_\lambda \equiv e^2 \int \frac{\tilde{\rho}_\lambda(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}([\tilde{\rho}_\lambda];\mathbf{r}) - e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - v_{xc}([\rho];\mathbf{r})$ involves $\tilde{\rho}_\lambda(\mathbf{r}) \equiv \sum_{i=1}^{N+1} |\tilde{\psi}_i^\lambda(\mathbf{r})|^2$ (filling the orbitals in order of increasing energy). Here, $\{\tilde{\psi}_i^\lambda(\mathbf{r})\}$ and $\{\epsilon_i^\lambda(N+1)\}$ are, respectively, the eigenstates and eigenvalues of H_λ:

$$H_\lambda \tilde{\psi}_i^\lambda(\mathbf{r}) = \epsilon_i^\lambda(N+1) \tilde{\psi}_i^\lambda(\mathbf{r}). \tag{8}$$

Equation (8) at $\lambda = 1$ is simply the KS equation for the $(N+1)$-electron system, as it can be verified that $\{\tilde{\psi}_i(\mathbf{r})\}$ and $\{\epsilon_i(N+1)\}$ are, respectively, the eigenstates and eigenvalues of $H_{\lambda=1}$. Therefore, $\epsilon_{N+1}(N+1) = \epsilon_{N+1}^{\lambda=1}(N+1)$.

Writing H'_λ, $\tilde{\psi}_i^\lambda(\mathbf{r})$, and $\epsilon_i^\lambda(N+1)$ as a power series in λ, we have

$$H'_\lambda = H'^{(0)} + \lambda H'^{(1)} + \lambda^2 H'^{(2)} + \cdots, \tag{9}$$

$$\tilde{\psi}_i^\lambda(\mathbf{r}) = \psi_i^{(0)}(\mathbf{r}) + \lambda\psi_i^{(1)}(\mathbf{r}) + \lambda^2\psi_i^{(2)}(\mathbf{r}) + \cdots, \tag{10}$$

$$\epsilon_i^\lambda(N+1) = \epsilon_i^{(0)} + \lambda\epsilon_i^{(1)} + \lambda^2\epsilon_i^{(2)} + \cdots. \tag{11}$$

Inserting Eqs. (7) and (9)–(11), into Eq. (8) gives

$$(H_{KS} + \lambda H'^{(0)} + \lambda^2 H'^{(1)} + \cdots)(\psi_i^{(0)} + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \cdots)$$
$$= (\epsilon_i^{(0)} + \lambda\epsilon_i^{(1)} + \lambda^2\epsilon_i^{(2)} + \cdots)(\psi_i^{(0)} + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \cdots). \tag{12}$$

Expanding Eq. (12) and comparing the coefficients of each power of λ yield an infinite series of simultaneous equations.

To zeroth order (λ^0) in Eq. (12), the equation is

$$H_{KS}\psi_i^{(0)}(\mathbf{r}) = \epsilon_i^{(0)}\psi_i^{(0)}(\mathbf{r}), \tag{13}$$

which is simply the KS equation for the N-electron system (i.e., the unperturbed system). We then have $\psi_i^{(0)}(\mathbf{r}) = \psi_i(\mathbf{r})$ and $\epsilon_i^{(0)} = \epsilon_i(N)$. Therefore, $\epsilon_{N+1}(N+1) = \epsilon_{N+1}^{\lambda=1}(N+1) \approx \epsilon_{N+1}^{(0)} = \epsilon_{N+1}(N)$. Correspondingly, $\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) \approx \epsilon_{N+1}(N) - \epsilon_{N+1}(N) = 0$ and $E_g = \Delta_{KS} + \Delta_{xc} \approx \Delta_{KS}$. Therefore, to obtain a nonvanishing Δ_{xc}, it is necessary to go beyond the zeroth-order theory.

To first order (λ^1) in Eq. (12) (see the Supplemental Material [40]), the first-order correction to the orbital energy is

$$\epsilon_i^{(1)} = \langle \psi_i^{(0)} \mid H'^{(0)} \mid \psi_i^{(0)} \rangle = \langle \psi_i \mid H'_{\lambda=0} \mid \psi_i \rangle, \tag{14}$$

and the first-order correction to the orbital is

$$\psi_i^{(1)}(\mathbf{r}) = \sum_{j \neq i} \frac{\langle \psi_j^{(0)} \mid H'^{(0)} \mid \psi_i^{(0)} \rangle}{\epsilon_i^{(0)} - \epsilon_j^{(0)}} \psi_j^{(0)}(\mathbf{r}). \tag{15}$$

Note that $\tilde{\rho}_{\lambda=0}(\mathbf{r}) = \sum_{i=1}^{N+1} |\tilde{\psi}_i^{\lambda=0}(\mathbf{r})|^2 = \sum_{i=1}^{N+1} |\psi_i^{(0)}(\mathbf{r})|^2 = \sum_{i=1}^{N+1} |\psi_i(\mathbf{r})|^2 = \rho(\mathbf{r}) + \rho_L(\mathbf{r})$, where $\rho_L(\mathbf{r}) \equiv |\psi_{N+1}(\mathbf{r})|^2$ is the KS LUMO density of the N-electron system. Consequently, we have

$$H'_{\lambda=0} = e^2 \int \frac{\rho_L(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xc}([\rho + \rho_L];\mathbf{r}) - v_{xc}([\rho];\mathbf{r}). \tag{16}$$

As $\epsilon_{N+1}(N+1) = \epsilon_{N+1}^{\lambda=1}(N+1) \approx \epsilon_{N+1}^{(0)} + \epsilon_{N+1}^{(1)}$, we have

$$\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) \approx \epsilon_{N+1}^{(1)}$$
$$= \langle \psi_{N+1} | H'_{\lambda=0} | \psi_{N+1} \rangle$$
$$= e^2 \iint \frac{\rho_L(\mathbf{r})\rho_L(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int \rho_L(\mathbf{r})\{v_{xc}([\rho + \rho_L];\mathbf{r})$$
$$- v_{xc}([\rho];\mathbf{r})\}d\mathbf{r} \tag{17}$$

and $E_g = \Delta_{KS} + \Delta_{xc} \approx \Delta_{KS} + \epsilon_{N+1}^{(1)}$. Equation (17) is a key result, showing that the DD can be approximately expressed as an explicit universal functional of $\rho(\mathbf{r})$ and $\rho_L(\mathbf{r})$ and can be calculated in the standard KS method without extra computational cost. Note that it can also be derived from Eq. (6) by assuming ("frozen orbital approximation") that

$$\tilde{\psi}_i(\mathbf{r}) \approx \psi_i(\mathbf{r}), \qquad i = 1, 2, 3, \ldots. \quad (18)$$

To second order (λ^2) in Eq. (12) (see the Supplemental Material [40]), the second-order correction to the orbital energy is

$$\epsilon_i^{(2)} = \langle \psi_i^{(0)} \mid H'^{(0)} \mid \psi_i^{(1)} \rangle + \langle \psi_i^{(0)} \mid H'^{(1)} \mid \psi_i^{(0)} \rangle$$

$$= \sum_{j \neq i} \frac{|\langle \psi_j \mid H'_{\lambda=0} \mid \psi_i \rangle|^2}{\epsilon_i(N) - \epsilon_j(N)} + \langle \psi_i \mid H'^{(1)} \mid \psi_i \rangle, \quad (19)$$

where

$$H'^{(1)} = \frac{\partial H'_\lambda}{\partial \lambda}\bigg|_{\lambda=0}$$

$$= \int \left\{ \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}([\tilde{\rho}_\lambda]; \mathbf{r})}{\delta \tilde{\rho}_\lambda(\mathbf{r}')} \right\} \frac{\partial \tilde{\rho}_\lambda(\mathbf{r}')}{\partial \lambda}\bigg|_{\lambda=0} d\mathbf{r}'$$

$$= \int \left\{ \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}([\rho + \rho_L]; \mathbf{r}, \mathbf{r}') \right\}$$

$$\times \left\{ 2 \sum_{i=1}^{N+1} \Re[\psi_i^*(\mathbf{r}')\psi_i^{(1)}(\mathbf{r}')] \right\} d\mathbf{r}'. \quad (20)$$

Here, $f_{xc}([\rho]; \mathbf{r}, \mathbf{r}') \equiv \delta v_{xc}([\rho]; \mathbf{r})/\delta \rho(\mathbf{r}')$ is the XC kernel, the asterisk denotes a complex conjugate, and $\Re[\cdots]$ denotes the real part of $[\cdots]$. From Eq. (19), we have

$$\epsilon_{N+1}^{(2)} = \sum_{j \neq N+1} \frac{|\langle \psi_j \mid H'_{\lambda=0} \mid \psi_{N+1} \rangle|^2}{\epsilon_{N+1}(N) - \epsilon_j(N)}$$

$$+ \langle \psi_{N+1} \mid H'^{(1)} \mid \psi_{N+1} \rangle. \quad (21)$$

Correspondingly, $\epsilon_{N+1}(N+1) = \epsilon_{N+1}^{\lambda=1}(N+1) \approx \epsilon_{N+1}^{(0)} + \epsilon_{N+1}^{(1)} + \epsilon_{N+1}^{(2)}$. This gives $\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) \approx \epsilon_{N+1}^{(1)} + \epsilon_{N+1}^{(2)}$ and $E_g = \Delta_{KS} + \Delta_{xc} \approx \Delta_{KS} + (\epsilon_{N+1}^{(1)} + \epsilon_{N+1}^{(2)})$.

Extending the process further, the HOMO energy of the $(N + 1)$-electron system can be obtained by summing up all the perturbation corrections to infinite order, i.e., $\epsilon_{N+1}(N+1) = \epsilon_{N+1}^{\lambda=1}(N+1) = \sum_{n=0}^\infty \epsilon_{N+1}^{(n)}$. Therefore, we can, in principle, obtain the exact $\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) = \sum_{n=1}^\infty \epsilon_{N+1}^{(n)}$ and the exact $E_g = \Delta_{KS} + \Delta_{xc} = \Delta_{KS} + \sum_{n=1}^\infty \epsilon_{N+1}^{(n)}$.

For any finite-order truncation of the above perturbation series, if two or more unperturbed states share the same energy, degenerate perturbation theory may be needed [36]. Since the concept of the perturbation to the unperturbed Hamiltonian H_{KS} remains valid, this scheme could be extended to estimate the Δ_{xc} (and hence the E_g) for the degenerate cases based on the corresponding degenerate perturbation theory.

As mentioned previously, the DD needs to be summed to the KS gap to give the fundamental gap. While the DD given by Eq. (4) should be the same as that given by Eq. (6) for the exact functional, this property may *no longer* hold true for an approximate functional. For example, for a LDA or a generalized gradient approximation, while the DD

given by Eq. (4) is shown to vanish [13,21,30], we emphasize that the DD can be *favorably restored* by Eq. (6) and subsequently approximated by Eq. (17). Although a more accurate approximation for the DD could be pursued by higher-order perturbation theory, we adopt the DD given by Eq. (17) (i.e., first-order correction) for simplicity. Accordingly, the fundamental gap is predicted by summing Eqs. (2) and (17) in our $\Delta_{KS} + \Delta_{xc}$ scheme.

Here, we examine the performance of various schemes in the prediction of the fundamental gaps for the FG115 database [20], which consists of 115 accurate reference values for the fundamental gaps of 18 atoms and 97 molecules at their experimental geometries. The fundamental gaps are calculated by our $\Delta_{KS} + \Delta_{xc}$ scheme, the Δ_{KS} scheme [by Eq. (2)], and the E_g scheme [by Eq. (5)], using the LDA [41] and LB94 [42] functionals and the 6-311++G(3df,3pd) basis set, with a development version of Q-CHEM 3.2 [43]. The error for each entry is defined as (error = theoretical value − reference value). The notation used for characterizing statistical errors is as follows: mean signed errors (MSEs), mean absolute errors (MAEs), and root-mean-square (rms) errors. Note that, for the Δ_{KS} or $\Delta_{KS} + \Delta_{xc}$ schemes, only one KS calculation for the N-electron system is required (i.e., applicable to solids), while, for the E_g scheme, which is the $\Delta_{KS} + \Delta_{xc}$ scheme with Δ_{xc} being exactly calculated by Eq. (6) (with no further approximations), two KS calculations for the N- and $(N + 1)$-electron systems are required (i.e., inapplicable to solids).

The calculated gaps are plotted against the reference values in Fig. 1 (for LDA) and Fig. 2 (for LB94). For both functionals, as the Δ_{KS} gaps are shown to be vanishingly small (some of them are even negative) for the small-gap (smaller than 10 eV) systems, the DDs are essential for the accurate prediction of the fundamental gaps. In fact,
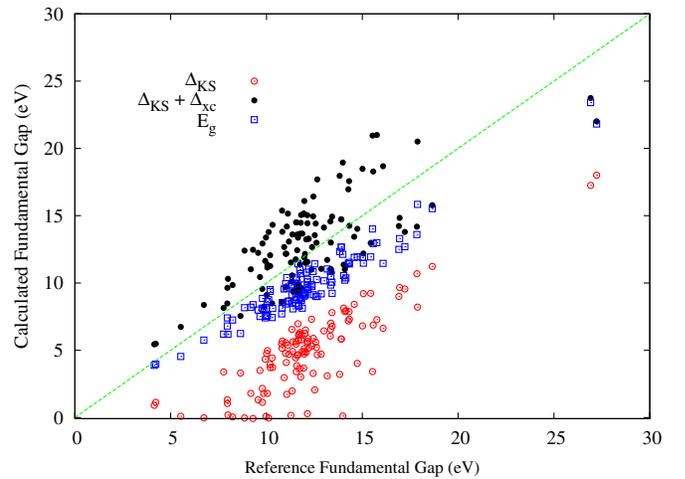
FIG. 1 (color online). Calculated versus reference fundamental gaps for the FG115 database [20]. The fundamental gaps are calculated by three schemes (see the text for details) using the LDA functional.
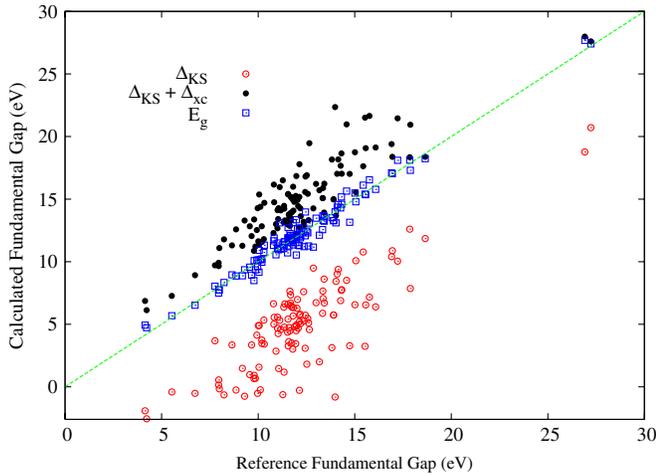
FIG. 2 (color online). Same as Fig. 1 but using the LB94 functional.

TABLE I. Statistical errors (in eV) of the 115 fundamental gaps of the FG115 database [20], calculated by three schemes (see the text for details) using the LDA and LB94 functionals.

Error	LDA			LB94		
	Δ_{KS}	$\Delta_{KS} + \Delta_{xc}$	E_g	Δ_{KS}	$\Delta_{KS} + \Delta_{xc}$	E_g
MSE	-7.22	0.78	-2.33	-7.20	2.73	0.03
MAE	7.22	2.11	2.33	7.20	2.74	0.47
rms	7.44	2.45	2.57	7.48	3.13	0.63

even for the large-gap (larger than 15 eV) systems, the DDs remain significant fractions of the fundamental gaps. As shown in Table I, the MAE associated with the $\Delta_{KS} + \Delta_{xc}$ or E_g schemes is more than three times smaller than that associated with the Δ_{KS} scheme [40].

Due to the use of the frozen orbital approximation [see Eq. (18)] in the evaluation of the DD, the $\Delta_{KS} + \Delta_{xc}$ gaps tend to be larger than the E_g gaps. For rare gas atoms (e.g., He, Ne, and Ar), where this approximation becomes excellent, the $\Delta_{KS} + \Delta_{xc}$ gaps are very close to the E_g gaps [40].

For LB94, the E_g gaps are in excellent agreement with the reference values, due to the correct asymptote of the LB94 potential, which is a key factor for the accurate prediction of the HOMO energies [28,37,38,42] and, via Eq. (5), the fundamental gaps. By contrast, for LDA, the E_g gaps tend to underestimate the reference values, due to the imbalanced self-interaction errors (as the LDA potential is asymptotically incorrect) in the predicted HOMO energies of the N- and $(N + 1)$-electron systems [2,4,28,37,38,42]. As the $\Delta_{KS} + \Delta_{xc}$ gaps tend to overestimate the E_g gaps, it appears that there is a fortuitous cancellation of errors in the predicted $\Delta_{KS} + \Delta_{xc}$ gaps, when compared with the reference values.

In conclusion, we have provided a systematic procedure for the direct evaluation of the DD, based on perturbation theory. The lowest-order estimate of the DD is an explicit universal functional of the ground-state density and the KS LUMO density [see Eq. (17)], presenting a simple, efficient, and nonempirical scheme for the direct evaluation of the DD in the standard KS method. The fundamental gap can be accurately predicted by the sum of the KS gap and the estimated DD. The validity and accuracy of this scheme have been demonstrated for a wide variety of atoms and molecules, extending the applicability of KS DFT to an area long believed to be beyond its reach. To further improve the accuracy of this scheme, a more accurate

functional and a more accurate approximation for the DD (based on higher-order perturbation theory) should be adopted, although this will necessarily be somewhat more expensive. Since the concepts of the DD and the perturbation to the unperturbed Hamiltonian H_{KS} are still valid for solid-state systems, this scheme could be extended to estimate the DD (a correction to the KS band gap) for solids, where the prediction of accurate fundamental band gaps is very challenging for KS DFT. Work in this direction is in progress.

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